

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
15 May 2003 (15.05.2003)

PCT

(10) International Publication Number
WO 03/040247 A1

(51) International Patent Classification⁷: **C09D 183/00**,
183/04, C09K 3/00, C08J 5/00, C08G 77/00, 65/00

(21) International Application Number: PCT/US02/28312

(22) International Filing Date:
5 September 2002 (05.09.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
10/007,556 8 November 2001 (08.11.2001) US

(71) Applicant: **3M INNOVATIVE PROPERTIES COMPANY** [US/US]; 3M Center, Post Office Box 33427, Saint Paul, MN 55133-3427 (US).

(72) Inventors: **MOORE, George G.I.**; Post Office Box 33427, Saint Paul, MN 55133-3427 (US). **DAMS, Rudolf J.**; Post Office Box 33427, Saint Paul, MN 55133-3427 (US). **FIEUWS, Franceska M.**; Post Office Box 33427, Saint Paul, MN 55133-3427 (US). **PIESSENS, Guido P.**; Post Office Box 33427, Saint Paul, MN 55133-3427 (US).

(74) Agents: **KOKKO, Kent S.**, et al.; Office of Intellectual Property Counsel, Post Office Box 33427, Saint Paul, MN 55133-3427 (US).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZM, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),

Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii)) for the following designations AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZM, ZW, ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG)

— as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii)) for the following designations AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZM, ZW, ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG)

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: COATING COMPOSITION COMPRISING A FLUOROCHEMICAL POLYETHER SILANE PARTIAL CONDENSATE AND USE THEREOF

(57) Abstract: A composition comprising a least one fluorochemical polyether silane compound having a polyfluoropolyether segment and at least two hydrolysable silane groups per molecule, one or more non-fluorinated compounds having at least two hydrolysable groups per molecule, and/or a partial condensate thereof, is disclosed. The composition provides durable water, oil and stain repellency to a substrate.

WO 03/040247 A1

**COATING COMPOSITION COMPRISING A FLUOROCHEMICAL
POLYETHER SILANE PARTIAL CONDENSATE AND USE THEREOF**

5 The present invention relates to a composition comprising at least one
fluorochemical polyether silane compound having a polyfluoropolyether segment and at
least two hydrolysable silane groups per molecule with one or more non-fluorinated
compounds having at least two hydrolysable groups per molecule. The present invention
also relates to a composition comprising a partial condensate resulting from a partial
10 condensation reaction between the fluorochemical polyether silane compound having a
polyfluoropolyether segment and at least two hydrolysable silane groups per molecule
with one or more non-fluorinated compounds having at least two hydrolysable groups per
molecule. The present invention also relates to the use of the compositions for providing
durable repellency to water, oil and stain to a substrate.

15 In the past, various efforts have been made to provide repellent properties to a
substrate. For example, U.S. 4,687,707 (=EP-A-0 166 363) describes a low reflectance,
transparent material having anti-soiling properties, which comprises a transparent
substrate having a coating comprising a thin layer of a condensation product of a fluorine
containing silicon compound having a polyfluorinated or perfluorinated carbon chain.

20 WO 99/03941 relates to a coating material comprising condensates of at least one
compound (A) of the general formula R_aMZ_b ($a = 0$ to 3 ; $b = 1$ to 4 ; $a + b = 3, 4$), and at
least one compound (B) of the general formula R'_xMZ_y ($x = 1$ to 3 ; $y = 1$ to 3 ; $x + y =$
 $3, 4$), wherein R is a non-hydrolysable organic group, M is an element selected from the
main groups III to V or from the subgroups II to IV of the periodic table of elements, Z is
25 a hydrolysable group, and at least one R' contains a perfluoropolyether structure separated
from M by at least two atoms, and at least one R is not equal to at least one R'. The
composition is used to provide oleophobic properties to substrates, such as porous
polymers.

30 U.S. 5,739,369 (=EP-A-0 738 771) relates to a water-soluble surface treating agent
comprising the reaction product of (A) a fluoroalkyl group-containing alkoxy silane with
(B) an amino-group-containing alkoxy silane and optionally further with (C) an alkyl

group-containing alkoxysilane. The agent is diluted with water to form a solution for treating glass and other substrates to impart thereto properties, such as water repellency.

US-A-5,919,886 relates to a fluorine-containing organo-silicon compound useful for obtaining elastomers and to room temperature curable silicon compositions containing the same compound.

U.S. 5,306,758 (=EP-A-0 433 070) describes fluorocarbon based, curable, crosslinkable compositions and coatings prepared therefrom that can be used to form low-surface energy release liners.

U.S. 5,922,787 (=EP-0 797 111) relates to a composition containing an alkoxy-silane compound having a perfluoropolyether group. The composition may be used for forming an anti-fouling film.

However, our findings indicate that while some of the previously known surface coatings may be capable of providing acceptable levels of initial repellent properties, a loss of repellency is often encountered due to abrasion of the coating.

Accordingly, it is desirable to provide a coating composition capable of providing a highly durable water, oil and/or stain repellent coating on a substrate. In particular, it is desirable to provide a durable coating wherein the initial, repellent properties are substantially maintained, even under abrading conditions. Further, the coating compositions preferably can be applied and used in an environmental friendly way and can be produced in a reliable, convenient and cost effective way. Additionally, the coatings desirably have a good durability against exposure to UV light, i.e. the repellency properties do not substantially degrade upon exposure to UV light. Furthermore, it is desirable to obtain optically clear coatings in particular when transparent substrates such as glass are to be treated with the compositions. It would also be desirable to obtain the desired repellency properties without the need for subjecting the coated substrate to a heat treatment at elevated temperature.

Summary of the Invention

In one aspect, the present invention provides a composition comprising (A) one or more fluorochemical polyether silane compound(s) having a polyfluoropolyether segment and at least two silane groups $-\text{Si}(\text{Y})_{3-x}(\text{R}^1)_x$ per molecule, wherein R^1 represents an alkyl

group, Y represents a hydrolysable group and x is 0 or 1; and (B) a substantial amount of one or more non-fluorinated compounds of an element M selected from the group consisting of Si, Ti, Zr, B, Al, Ge, V, Pb, Sn and Zn and having at least two hydrolysable groups per molecule. In another aspect the present invention provides the reaction product of (A) and (B).

In a further aspect, the present invention provides a composition derivable from a partial condensation of the above defined composition. By "partial condensation" and "partial condensate" in connection with the present invention is meant that some of the hydrolysable groups in the mixture have reacted while leaving a substantial amount of hydrolysable groups available for a condensation reaction. Typically, a partial condensate means that at least 20%, preferably at least 30%, more preferably at least 50% of the hydrolysable groups are still available for condensation reaction.

In a still further aspect, the present invention also provides a method for treating a substrate, comprising the step of applying to at least a portion of the surface of the substrate the compositions as defined above. The fluorochemical compositions of the present invention can be used to treat substrates and are capable of rendering such substrates oil and water repellent and/or to provide stain repellency thereto.

The compositions are generally effective at low levels of application and have good durability. The compositions are particularly useful for rendering substrates such as ceramics, glass, inox and chromated steel, repellent to water and/or oil.

In a further aspect, the present invention also provides for compositions from which a composition as defined above can be readily prepared. Such compositions comprise components (A) and (B) and are substantially free of water. By substantially free of water is meant that the compositions do not contain water or the amount of water is so low that reaction between components (A) and (B) does not occur in such composition. Preferably, these compositions are also free of acid or base catalyst and will conveniently contain an amount of organic solvent so as to obtain a homogeneous mixture.

By the term "homogeneous mixture" in connection with the present invention is meant that the composition is stable, for at least 24 hours, preferably 1 month, at room temperature. Some haziness may occur, however without substantial precipitation or phase separation occurring.

The term "hydrolysable group" in connection with the present invention refers to a group which either is directly capable of undergoing condensation reactions under appropriate conditions or which is capable of hydrolyzing under appropriate conditions, thereby yielding a compound, which is capable of undergoing condensation reactions.

5 Appropriate conditions include acidic or basic aqueous conditions, optionally in the presence of a condensation catalyst.

Accordingly, the term "non-hydrolysable group" as used in the present invention refers to a group not capable of either directly undergoing condensation reactions under appropriate conditions or of hydrolyzing under the conditions listed above for hydrolyzing the hydrolyzable groups.

The term "substantial amount" of a compound as used herein refers to an amount of a compound greater than a catalytic amount of that compound necessary for promoting a certain reaction (e.g., condensation reactions). Accordingly, a composition comprising a substantial amount of that compound generally allows the compound to act as a reactant
15 such that the resulting product is formed of at least part of that compound.

Detailed Description

Component (A) comprises at least one fluorochemical polyether silane compound
20 having a polyfluoropolyether segment and at least two silane groups $-\text{Si}(\text{Y})_{3-x}(\text{R}^1)_x$ per molecule, wherein R^1 represents an alkyl group (for example a C_1 - C_8 , preferably C_1 - C_4 primary or secondary alkyl group), Y represents a hydrolysable group and x is 0 or 1.

Preferably, component (A) is a fluorochemical polyether silane compound according to formula (I)

25
$$\text{R}_f[\text{Q}-\text{C}(\text{R})_2-\text{Si}(\text{Y})_{3-x}(\text{R}^1)_x]_z \quad (\text{I})$$

wherein R_f represents a multivalent polyfluoropolyether segment, Q represents an organic divalent linking group, R^1 represents an alkyl group (preferably containing 1 to 8, more preferably 1 to 4 carbon atoms), Y represents a hydrolysable group; R represents hydrogen or an alkyl group of 1 to 4 carbon atoms and the R groups may be the same or different, x
30 is 0 or 1 and z is 2, 3 or 4. Preferably both R groups are hydrogens.

The hydrolysable groups Y may be the same or different and are generally capable of hydrolyzing under appropriate conditions, for example under acidic or basic aqueous

conditions, such that the fluorochemical silane compound can then undergo condensation reactions. Preferably, the hydrolysable groups upon hydrolysis yield groups capable of undergoing condensation reactions, such as silanol groups.

Examples of hydrolysable groups include halide groups, such as chlorine, bromine, iodine or fluorine, alkoxy groups $-OR'$ (wherein R' represents a lower alkyl group, preferably containing 1 to 6, more preferably 1 to 4 carbon atoms and which may optionally be substituted by one or more halogen atoms), acyloxy groups $-O(CO)-R''$ (wherein R'' represents a lower alkyl group, preferably containing 1 to 6, more preferably 1 to 4 carbon atoms, which may be optionally substituted by one or more halogen atoms), aryloxy groups $-OR'''$ (wherein R''' represents an aryl moiety, preferably containing 6 to 12, more preferably containing 6 to 10 carbon atoms, which may be optionally substituted by one or more substituents independently selected from halogens, and C_1 - C_4 alkyl groups which may optionally be substituted by one or more halogen atoms). In the above formulae R' , R'' , and R''' may include branched structures.

Suitable hydrolysable groups also include polyoxyalkylene groups of the formula $-O-A-R^3$ wherein A is a divalent hydrophilic group (a) having the formula $(CHR^4-CH_2O)_q$ wherein q is a number having a value of 1 to 40, preferably 2 to 10, R^4 is hydrogen or methyl, and at least 70% of R^4 is hydrogen, and R^3 independently is hydrogen or a lower alkyl group having 1 to 4 carbon atoms, such as disclosed in U.S. Pat. No. 5,274,159, incorporated herein by reference.

Specific examples of hydrolysable groups include methoxy, ethoxy and propoxy groups, chlorine and an acetoxy group. Particularly preferred hydrolysable groups include C_1 - C_4 alkoxy groups, such as methoxy and ethoxy groups. C_2 - C_4 alkoxy groups are preferred in case it is desired to obtain clear coatings on a substrate.

The divalent polyfluoropolyether group R_f in the above formula (I), representing the fluorinated polyether silane, can include linear, branched, and/or cyclic structures, that may be saturated or unsaturated, and containing one or more catenary oxygen atoms (i.e. one or more non-adjacent $-CF_2-$ groups may be replaced by $-O-$ groups). R_f preferably is a perfluorinated group (i.e., all C-H bonds are replaced by C-F bonds). More preferably, it includes perfluorinated repeating units selected from the group of $-(C_nF_{2n}O)-$, $-(CF(Z)O)-$,

-(CF(Z)C_nF_{2n}O)-, -(C_nF_{2n}CF(Z)O)-, -(CF₂CF(Z)O)-, and combinations thereof, wherein the repeating units generally may be randomly, blocky or alternating arranged, and optionally can include -(C_nF_{2n})- and -(CF(Z))- units and wherein n is a number from 1 to 12 inclusive, preferably from 1 to 4 inclusive. R_f may also comprise cyclic perfluoro groups, for example cyclic -C₆F₁₀- groups.

In these repeating units Z is a perfluoroalkyl group, an oxygen-containing perfluoroalkyl group, a perfluoroalkoxy group, or an oxygen-substituted perfluoroalkoxy group, all of which can be linear, branched, or cyclic, and preferably have about 1 to about 9 carbon atoms and 0 to about 4 oxygen atoms. Examples of polyfluoropolyethers containing polymeric moieties made of these repeating units are disclosed in U.S. Pat. No. 5,306,758 (Pellerite).

In one embodiment, approximate average structures for a divalent perfluoropolyether group include -CF₂O(CF₂O)_m(C₂F₄O)_pCF₂-, wherein an average value for m is 0 to about 50 and an average value for p is 0 to about 50, with the proviso that both m and p are not simultaneously 0, -CF(CF₃)-(OCF₂CF(CF₃))_pO-R_f'- O(CF(CF₃)CF₂O)_pCF(CF₃)-, -CF₂O(C₂F₄O)_pCF₂-, and -(CF₂)₃O(C₄F₈O)_p(CF₂)₃-, wherein R_f' is a divalent, perfluoroalkylene group containing one or more carbons and optionally catenary O or N. The values of m and p in these approximate average structures can vary. Preferably, an average value of m is within a range of about 1 to about 50, and an average value of p is within a range of about 3 to about 40. As these are polymeric materials, such compounds exist as mixtures upon synthesis, which are suitable for use. The repeat units generally may be positioned in a random, blocked or alternating arrangement.

As synthesized, these structures typically include a mixture of polymeric units. The approximate average structure is the approximate average of the mixture of structures. Further, the distribution of perfluorinated repeating units may be regular or random.

The divalent linking group Q may be the same or different and can include linear, branched, or cyclic structures, that may be saturated or unsaturated, and preferably contains 1 to 15 atoms. The group Q can contain one or more heteroatoms (e.g., oxygen, nitrogen, or sulfur) and/or one or more functional groups (e.g., carbonyl, amide, urethane or sulfonamide). It can also be substituted with one or more halogen atoms (preferably, fluorine atoms), although this is less desirable, as this might lead to instability of the

compound. The divalent linking group Q preferably is substantially stable against hydrolysis.

For example, Q may be a saturated or unsaturated hydrocarbon group typically including 1 to 15 carbons atoms. Preferably Q is a linear hydrocarbon group preferably containing 1 to 10 carbon atoms, and optionally containing 1 to 4 heteroatoms and/or 1 to 4 functional groups, and more preferably, containing at least one functional group.

Suitable linking groups Q include the following structures in addition to a covalent bond. For the purposes of this list, each k is independently an integer from 0 to about 20, k' is independently an integer from 0 to 20, preferably from 2 to 12 and most preferably from 2 to 6, R₁' is hydrogen, phenyl, or alkyl of 1 to about 4 carbon atoms, and R₂' is alkyl of 1 to about 20 carbon atoms

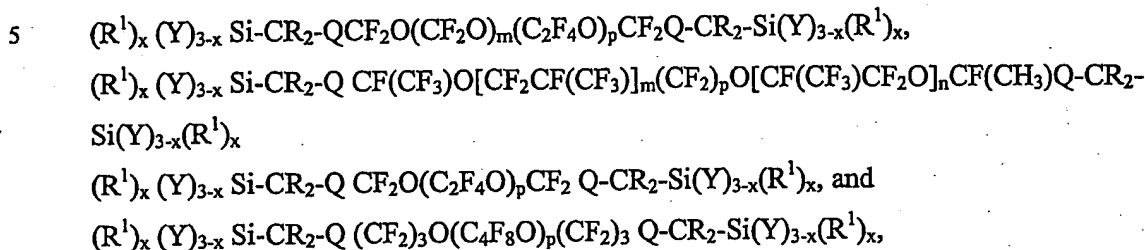
-SO ₂ NR ₁ '(CH ₂) _k O(O)C-	-CONR ₁ '(CH ₂) _k O(O)C-
-(CH ₂) _k O(O)C-	-CH ₂ CH(OR ₂ ')CH ₂ O(O)C-
-(CH ₂) _k C(O)O(CH ₂) _{k'} -	-(CH ₂) _k SC(O)-
-(CH ₂) _k O(CH ₂) _k O(O)C-	-(CH ₂) _k S(CH ₂) _k O(O)C-
-(CH ₂) _k SO ₂ (CH ₂) _k O(O)C-	-(CH ₂) _k S(CH ₂) _k OC(O)-
-(CH ₂) _k SO ₂ NR ₁ '(CH ₂) _k O(O)C-	-(CH ₂) _k SO ₂ -
-SO ₂ NR ₁ '(CH ₂) _k O(CH ₂) _{k'} -	-SO ₂ NR ₁ '(CH ₂) _k -
-(CH ₂) _k O(CH ₂) _k C(O)O(CH ₂) _{k'} -	-(CH ₂) _k SO ₂ NR ₁ '(CH ₂) _k C(O)O(CH ₂) _{k'} -
-(CH ₂) _k SO ₂ (CH ₂) _k C(O)O(CH ₂) _{k'} -	-CONR ₁ '(CH ₂) _k C(O)O(CH ₂) _{k'} -
-(CH ₂) _k S(CH ₂) _k C(O)O(CH ₂) _{k'} -	-CH ₂ CH(OR ₂ ')CH ₂ C(O)O(CH ₂) _{k'} -
-SO ₂ NR ₁ '(CH ₂) _k C(O)O(CH ₂) _{k'} -	-(CH ₂) _k O(CH ₂) _{k'} -
-OC(O)NR ₁ '(CH ₂) _k -	-(CH ₂) _k NR ₁ '-
-C _k H _{2k} -OC(O)NH-	-C _k H _{2k} -NR ₁ 'C(O)NH(CH ₂) _{k'} -,
-(CH ₂) _k NR ₁ 'C(O)O(CH ₂) _{k'} -, and	-(CH ₂) _k -

Preferred linking groups Q are -C(O)NH(CH₂)₂- and -OC(O)NH(CH₂)₂-.

Compounds of formula (I) that are conveniently used, generally have a molecular weight of at least about 650, and preferably, at least about 1000. It will be understood,

with respect to the description of formula I, that the composition comprises mixtures of compounds and therefore mixtures of molecular weights.

Examples of preferred fluorinated disilanes (A) include, but are not limited to, the following approximate average structures:

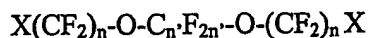


10 Preferably, in each fluorinated polyether silane, Q contains a nitrogen atom. More preferably, at least one Q-CR₂-Si(Y)_{3-x}(R¹)_x group per molecule is C(O)NH(CH₂)₃Si(OR)₃ or OC(O)NH(CH₂)₃Si(OR)₃ (wherein R is methyl, ethyl, polyethyleneoxy or mixtures thereof).

The compounds of formula (I) can be synthesized using standard techniques. For 15 example, commercially available or readily synthesized perfluoropolyether esters (or function derivative thereof) can be combined with a functionalized alkoxysilane, such as a 3-aminopropylalkoxysilane, according to US-A-3,810,874 (Mitsch et al.). It will be understood that functional groups other than esters may be used with equal facility to incorporate silane groups into a perfluoropolyether.

20 In accordance with a particular embodiment of the present invention, such perfluoropolyether esters may be prepared through direct fluorination of a hydrocarbon polyether diester. Direct fluorination involves contacting the hydrocarbon polyether diester with F₂. Accordingly, the hydrogen atoms on the hydrocarbon polyether diester will be replaced with fluorine atoms thereby generally resulting in the corresponding 25 perfluoropolyether diester. Direct fluorination methods are disclosed in, for example, US Patent Nos. 5,578,278 and 5,658,962, which are incorporated herein by reference.

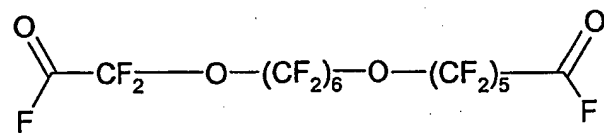
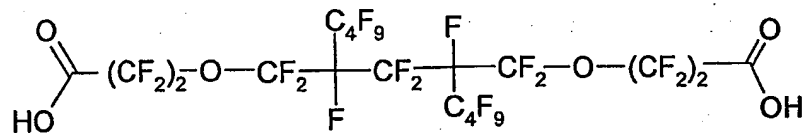
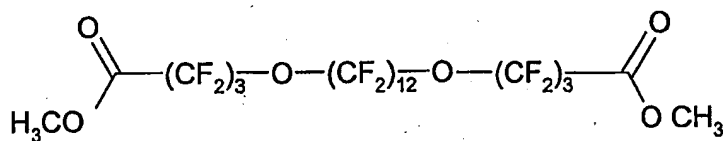
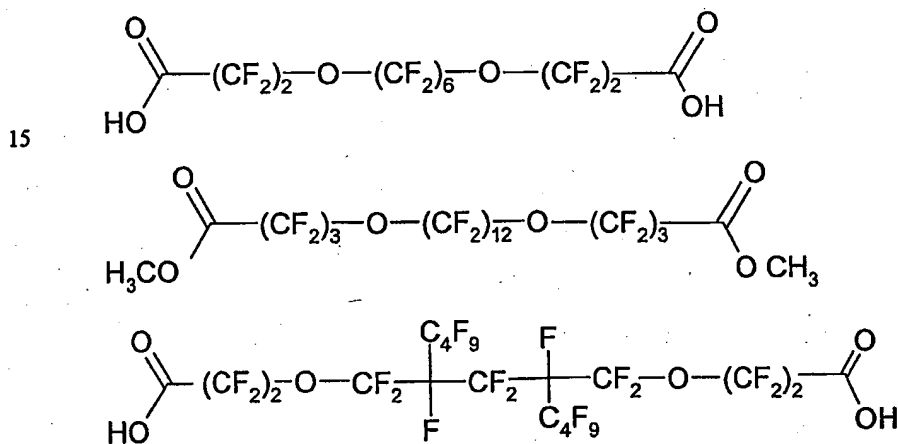
Examples of intermediates suitable for use in the preparation of fluorochemical polyether silanes may be represented by the general formula R_f-X_z, wherein R_f is as 30 previously defined for Formula I and z is 2, 3 or 4. A particularly useful intermediate may be represented by the general formula



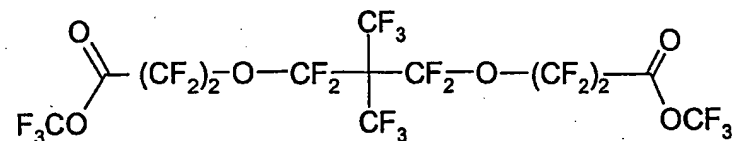
where n is in the range of 1 to 6, and preferably in the range of 1 to 3; n' is in the range of 5 to 12, and preferably in the range of 5 to 7, X is selected from the group consisting of -COOH, -COOM_{1/v}, -COONH₄, -COOR, -CH₂OH, -COF, -COCl, -COR, CONR'R',
 5 -CH₂NH₂, -CH₂NCO, -CN, -CH₂OSO₂R, -CH₂OCOR, -OC(O)CH₃, -CH₂OCOCR'=CH₂, -CONH(CH₂)_mSi(OR)₃, and -CH₂O(CH₂)_mSi(OR)₃;

where M is a metal atom having a valence "v" of 1 to 4, each R is independently selected from the group consisting of alkyl groups having from 1 to 14 carbon atoms, fluoroalkyl groups having from 1 to 14 carbon atoms, aryl groups having from 6 to 10 ring-carbon
 10 atoms, and heteroatom-containing groups having from 1 to 14 carbon atoms, and m is an integer in the range from 1 to 11; R' is independently H or R with the proviso R' is not a fluoroalkyl group.

Specific structures are exemplified by:

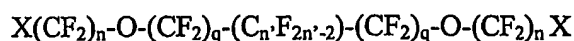


20 and



It will be understood with respect to the above novel structures, that other functional groups may be substituted for those depicted. For examples, the $-\text{CO}_2\text{H}$ group may be substituted by $-\text{COOM}_{1/v}$, $-\text{COONH}_4$, $-\text{COOR}$, $-\text{CH}_2\text{OH}$, $-\text{COF}$, $-\text{COCl}$, $-\text{COR}$, $\text{CONR}'\text{R}'$, $-\text{CH}_2\text{NH}_2$, $-\text{CH}_2\text{NCO}$, $-\text{CN}$, $-\text{CH}_2\text{OSO}_2\text{R}$, $-\text{CH}_2\text{OCOR}$, $-\text{OC}(\text{O})\text{CH}_3$,
 5 $-\text{CH}_2\text{OCOCR}'=\text{CH}_2$, $-\text{CONH}(\text{CH}_2)_m\text{Si}(\text{OR})_3$, and $-\text{CH}_2\text{O}(\text{CH}_2)_m\text{Si}(\text{OR})_3$ as previously described.

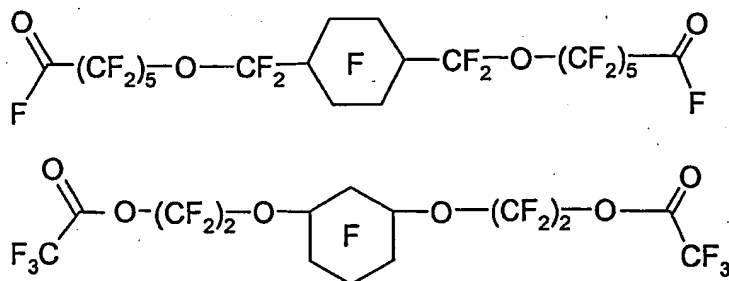
An additional embodiment is a composition comprising



10

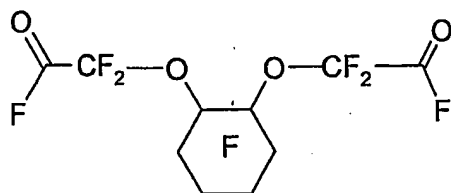
where n is in the range of 1 to 6, and preferably in the range of 1 to 3; $\text{C}_n\text{F}_{2n'-2}$ represents a cycloalkylene moiety where n' is in the range of 5 to 12, and preferably in the range of 6 to 8, X is selected from the group consisting of $-\text{COOH}$, $-\text{COOM}_{1/v}$, $-\text{COONH}_4$, $-\text{COOR}$, $-\text{CH}_2\text{OH}$, $-\text{COF}$, $-\text{COCl}$, $-\text{COR}'$, $\text{CONR}'\text{R}'$, $-\text{CH}_2\text{NH}_2$, $-\text{CH}_2\text{NCO}$, $-\text{CN}$, $-\text{CH}_2\text{OSO}_2\text{R}$,
 15 $-\text{CH}_2\text{OCOR}$, $-\text{OC}(\text{O})\text{CH}_3$, $-\text{CH}_2\text{OCOCR}'=\text{CH}_2$, $-\text{CONH}(\text{CH}_2)_m\text{Si}(\text{OR})_3$, $-\text{CH}_2\text{O}(\text{CH}_2)_m\text{Si}(\text{OR})_3$; where M is a metal atom having a valence " v " of 1 to 4, each R is independently selected from the group consisting of alkyl groups having from 1 to 14 carbon atoms, fluoroalkyl groups having from 1 to 14 carbon atoms, aryl groups having from 6 to 10 ring-carbon atoms, and heteroatom-containing groups having from 1 to 14
 20 carbon atoms, q is 0 or 1, and m is an integer in the range from 1 to 11; R' is independently H or R with the proviso R' is not a fluoroalkyl group.

Specific perfluorinated cycloalkylene-containing structures are exemplified by:



25

and

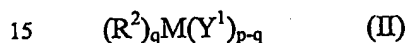


In an alternative method, perfluoropolyetherdiols can be reacted with a functionalized alkoxysilane, such as 3-trimethoxysilylpropylisocyanate. Modifications of this method are described in the Examples. Such materials may or may not need to be purified before use in a treatment composition.

In the present invention, mixtures of compounds (A) and/or mixtures of compounds (B) may be used.

Component (B) as used in the present invention comprises one or more non-fluorinated compounds of an element M selected from the group consisting of Si, Ti, Zr, B, Al, Ge, V, Pb, Sn and Zn having at least two hydrolysable groups per molecule. Preferably, the hydrolysable groups are directly bonded to the element M.

In one embodiment of the present invention, component (B) comprises a compound according to the formula (II)



wherein R^2 represents a non-hydrolysable group, M represents an element of valency $p+q$, selected from the group consisting of Si, Ti, Zr, B, Al, Ge, V, Pb, Sn and Zn, p is 3 or 4 depending on the valence of M, q is 0, 1 or 2, and Y^1 represents a hydrolysable group.

The hydrolysable groups present in component (B) may be the same or different and are generally capable of hydrolyzing under appropriate conditions, for example under acidic or basic aqueous conditions, such that component (B) can undergo condensation reactions. Preferably, the hydrolysable groups upon hydrolysis yield groups capable of undergoing condensation reactions, such as hydroxyl groups.

Typical and preferred examples of hydrolysable groups include those as described with respect to component (A). Preferably, component (B) includes tetra-, tri- or dialkoxy (preferably containing 1 to 4 carbon atoms) compounds.

The non-hydrolysable groups R^2 may be the same or different and are generally not capable of hydrolyzing under the conditions listed above. For example, the non-hydrolysable groups R^2 may be independently selected from a hydrocarbon group, for

example a C₁-C₃₀ alkyl group, which may be straight chained or branched and may include one or more aliphatic, cyclic hydrocarbon structures, a C₆-C₃₀ aryl group (optionally substituted by one or more substituents selected from halogens and C₁-C₄ alkyl groups), or a C₇-C₃₀ aralkyl group.

5 In one embodiment the non-hydrolysable groups R² are independently selected from a hydrocarbon group, for example a C₁-C₃₀ alkyl group and a C₆-C₂₀ aryl group (optionally substituted by one or more substituents selected from halogens and C₁-C₄ alkyl groups).

Preferred compounds (B) include those in which M is Ti, Zr, Si and Al.
10 Representative examples of component (B) include tetramethoxysilane, tetra ethoxysilane, methyl triethoxysilane, dimethyldiethoxysilane, octadecyltriethoxysilane, methyl trichlorosilane, tetra-methyl orthotitanate, tetra ethyl orthotitanate, tetra-iso-propyl orthotitanate, tetra-n-propyl orthotitanate, tetraethyl zirconate, tetra-iso-propyl zirconate tetra-n-propyl zirconate and the like. More preferred compounds include C₁-C₄ alkoxy
15 derivatives of Si, Ti and Zr. Particularly preferred compounds (B) include tetraethoxysilane. Single compounds or mixtures of compounds (B) may be used.

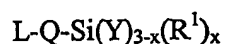
Optionally, the composition may comprise one or more crosslinking agents (C), in order to further increase the durability of the coating. Component (C) may be selected from compounds with additional functionality from those of components (A) and (B). For
20 example, component (C) may comprise a compound of an element M¹ that is selected from the group consisting of Si, Ti, Zr, B, Al, Ge, V, Pb, Sn and Zn having at least one hydrolysable group and at least one reactive functional group per molecule that is capable of engaging in a crosslinking reaction. Preferably, said at least one hydrolysable group is directly bonded to the element M¹.

25 Suitable and preferred hydrolysable groups include those groups mentioned with respect to component (A). If component (C) includes more than one hydrolysable groups, these may be the same or different. Particularly preferred hydrolysable groups are selected from C₁-C₄ alkoxy groups, such as methoxy, ethoxy, iso- and (preferably) n-propoxy, or iso- and (preferably) n-butoxy groups.

30 The reactive functional group is a group which is capable of engaging in a crosslinking reaction so as to provide further crosslinking functionality to the polycondensation product that can be obtained from components (A), (B) and (C). The

crosslinking reaction may involve for example irradiation, heating or a combination thereof. If component (C) includes more than one reactive functional groups, these groups may be the same or different. Of these, free radically polymerizable groups, such as vinyl, acrylate or methacrylate groups, are particularly preferred reactive functional groups.

5 A preferred crosslinking agent can be represented by formula (IV) :



wherein

L represents a reactive functional group that may react by condensation or addition reactions such as an amino group, an epoxy group, a mercaptan or an anhydride group or
10 by free-radical polymerization; and

Q, Y and R¹ are as described for formula I, and x is 0, 1 or 2.

For formula V, preferably Q is an alkylene (preferably containing 1 to 10, more preferably containing 1 to 6 carbon atoms), an arylene (preferably containing 6 to 20 carbon atoms which may be substituted by one or more C₁-C₄ alkyl groups, halogen atoms
15 or mixtures thereof), an oxyalkylene group of the formula (-O-R-)_n, wherein R is independently selected from a divalent, straight chained or branched lower alkyl group (preferably containing 1 to 6 carbon atoms) and n is an integer from 1 to 20.

For formula IV, preferably R¹ independently represents an alkyl group, preferably a C₁-C₈ alkyl group (such as methyl, ethyl or propyl) or an C₁-C₈ alkyl group containing a
20 cyclic hydrocarbon structure (such as cycloalkyl such as cyclohexyl or cyclopentyl), an aryl group (preferably containing 6 to 20 carbon atoms which may optionally be substituted by one or more C₁-C₄ alkyl groups or halogens or mixtures thereof, such as phenyl), an alkylaryl group (preferably containing 7 to 12 carbon atoms) or an aralkyl group (preferably containing 7 to 12 carbon atoms).

25 For formula IV, Y is hydrolysable group. Suitable and preferred examples of hydrolysable groups include those groups as mentioned with respect to component (A), formula I. Particularly preferred hydrolysable groups include alkoxy groups (preferably containing 1 to 4 carbon atoms), such as methoxy and ethoxy groups.

Particularly preferred reactive compounds according to formula (IV), in which the
30 reactive functional group L is one that reacts by addition or condensation reactions, include epoxypropyltrimethoxysilane, bis(3-aminopropyltrimethoxysilyl)amine and aminopropyltrimethoxysilane.

Alternatively L may be a reactive functional group that is a free radically polymerizable group that typically contains an ethylenically unsaturated group capable of undergoing a free radical polymerization. Suitable free radically polymerizable groups L include, for example, moieties derived from vinyl ethers, vinyl esters, allyl esters, vinyl ketones, styrene, vinyl amide, acrylamides, maleates, fumarates, acrylates and methacrylates. Of these, the esters and amides of alpha, beta unsaturated acids, such as the acrylates and methacrylates are preferred.

Where L is a free radically polymerizable group the organic divalent linking group Q may contain from 1 to about 20, preferably from 1 to 10 carbon atoms. Q can optionally contain oxygen, nitrogen, or sulfur-containing groups or a combination thereof. Examples of suitable linking groups Q include straight chain, branched chain or cyclic alkylene (preferably containing 2 to 20 carbon atoms), arylene (preferably containing 6 to 20 carbon atoms), aralkylene (preferably containing 7 to 20 carbon atoms), oxyalkylene, carbonyloxyalkylene, oxycarboxyalkylene, carboxyamidoalkylene, urethanealkylene, ureylenealkylene and combinations thereof.

Preferred linking groups Q for Formula IV are selected from the group consisting of alkylene (preferably containing 2 to 20, more preferably 2 to 10 carbon atoms), oxyalkylene (preferably containing 2 to 20 carbon atoms and 1 to 10 oxygen atoms) and carbonyloxyalkylene (preferably containing 3 to 20 carbon atoms).

Examples of compounds according to formula (IV), wherein L is a free radically polymerizable group include vinyltrichlorosilane, vinyltrimethoxysilane, vinyltriethoxysilane and alkoxyfunctionalised acrylates or methacrylates, such as methacryloyloxypropyl trimethoxysilane.

The presence of such reactive functional groups, preferably reactive unsaturated groups in the corresponding polycondensates is advantageous in that following the coating of the composition onto a substrate a two-fold curing can be carried out, i.e. a thermal or photochemically induced linking of the unsaturated organic radicals through radical polymerization and a thermal completion of the polycondensation (e.g. by elimination of water from groups M-OH still present). In the case an unsaturated compound is used, additionally a catalyst should typically be present for the thermal and/or photochemically induced curing of the coating composition applied onto a suitable substrate. Particularly preferred is the addition of a photopolymerization initiator. Such initiators are

commercially available and include e.g. Irgacure® 184 (1-hydroxycyclohexyl phenyl ketone), Irgacure®500 (1-hydroxycyclohexyl phenyl ketone, benzophenone), and other photo-initiators of the Irgacure®-type available from Ciba-Geigy ; Darocur®-type photo-initiators, available from Merck, benzophenone and the like.

5 Examples of optionally employed thermal initiators are known to those skilled in the art and include, among others, organic peroxides in the form of diacyl peroxides, peroxydicarbonates, alkyl peresters, dialkyl peroxides, perketals, ketone peroxides and alkyl hydroperoxides. Specific examples of such thermal initiators are dibenzoyl peroxide, tert-butyl perbenzoate and azobisisobutyronitrile. These initiators are added to the coating
10 composition in amounts known to one skilled in the art. Typically the initiator will be added in an amount between 0.1 and 2% by weight, based on the compounds according to formula IV.

 The compositions may further contain additives that provide the coating with additional properties, such as antimicrobial properties. Examples include $[C_{18}H_{37}N(CH_3)_2(CH_2)_3Si(OCH_3)_3]^+Cl^-$. However, the addition of ionic hydrolysing the hydrolysable
15 groups present in the components and carrying out additives is preferably kept below about 10% by weight, in order not to adversely affect the water repellency properties of the composition.

 According to the present invention, it is preferred that the weight ratio of
20 compounds (A) to compounds (B) in the fluorochemical composition is 1:1 to 1:20 and particularly preferred 1:1 to 1:10. The composition of the present invention comprises a substantial amount of component (B), i.e. an amount greater than a catalytic amount. Typically, component (B) comprises more than 10 weight percent and more preferably more than 25 weight percent based on the total weight of the components used. In a
25 particularly preferred embodiment, component (B) comprises more than 50 weight percent based on the total weight of the components used. Compound (C) can be used between 0 and 50%, preferably between 0 and 35% by weight, based on the total weight of the components used.

 While the benefits of reacting components A and B (optionally with C) extend over
30 a wide range of compositions, good initial repellency is achieved for coatings despite relatively low levels of the fluorochemical polyether silane (component A). Therefore a preferred embodiment of this invention employs the relatively expensive fluorosilane at 5-

20% wt.%, giving an economic advantage to the compositions of this invention over other fluorinated coatings. Additionally, compositions of 5-20 wt. % component A were quite surprisingly more durable in maintaining repellency after abrasion of a coated surface.

5 In one embodiment, a composition comprising components (A) and (B) and optionally (C), sufficient solvent, water, and acid or base catalyst may be combined and coated onto a suitable substrate. When such a coating is applied to the substrate shortly after its preparation, components (A) and (B) and optionally (C) will generally not have undergone a condensation reaction or if condensation has occurred the amount thereof will be low. Generally, the amount of condensation that takes place prior to coating will
10 depend on the concentration and nature of components (A) and (B) and optionally (C), the temperature and the time between preparation of the coating composition and the coating of the substrate. Generally, the coating composition will contain components (A) and (B) each in amounts between 0.01% by weight and 5% by weight and the coating is typically applied within about 3 to 8 hours from its preparation. The present invention however does
15 not exclude the possibility of coating a composition in which partial condensates have formed. Typically, compositions comprising partial condensates may form when the aforementioned coating composition is left for some time before coating, for example for more than 1 hour. Nevertheless, the coating composition should be applied to the substrate before the condensation reaction proceeds towards completion.

20 Preferably, the amount of water will be between 0.1 and 20 % by weight of the total composition, more preferably between 1 and 10% by weight. In addition to water, an organic or inorganic acid or base catalyst should preferably be used in the coating composition.

25 Organic acid catalysts include acetic acid, citric acid, formic acid, triflic acid, perfluorobutyric acid and the like. Examples of inorganic acids include sulphuric acid, hydrochloric acid and the like. Examples of useful base catalysts include sodium hydroxide, potassium hydroxide and triethylamine. The acid or base catalyst will generally be used in amounts between about 0.01 and 10%, more preferably between 0.05 and 5% by weight of the total composition.

30 The composition of the present invention typically includes one or more organic solvents. The organic solvent or blend of organic solvents used must be capable of dissolving a mixture of compounds (A), (B) and optionally (C) and any partial condensate

that may form as a result of partial condensation of (A), (B) and optionally (C). Preferably, the organic solvent or blend of organic solvents used is capable of dissolving at least 0.01% of compounds (A), (B), (C) and/or partial condensates thereof. Furthermore, the solvent or mixture of solvents preferably has a solubility for water of at least 0.1%, preferably 1% by weight and a solubility for the acid or base catalyst of at least 0.01%, preferably 0.1% by weight. If the organic solvent or mixture of organic solvents do not meet these criteria, it may not be possible to obtain a homogeneous mixture of the fluorinated polycondensate, solvent(s), water and catalyst.

Suitable organic solvents, or mixtures of solvents can be selected from aliphatic alcohols (preferably containing 1 to 6 carbon atoms), such as methanol, ethanol, isopropylalcohol; ketones such as acetone or methyl ethyl ketone; esters, such as ethyl acetate, methylformate and ethers, such as diethyl ether. Particularly preferred solvents include ethanol and acetone.

Fluorinated solvents may be used in combination with the organic solvents in order to improve solubility of the starting compounds and/or the partial condensate. Such fluorinated solvents will generally not be suitable for use on their own because they will generally not meet the requirements of solubility for water and acid or base unless they additionally contain hydrophilic groups such as $\text{CF}_3\text{CH}_2\text{OH}$.

Examples of fluorinated solvents include fluorinated hydrocarbons, such as perfluorohexane or perfluorooctane, available from 3M; partially fluorinated hydrocarbons, such as pentafluorobutane, available from Solvay, or $\text{CF}_3\text{CFHCFHCF}_2\text{CF}_3$, available from DuPont; hydrofluoroethers, such as methyl perfluorobutyl ether or ethyl perfluorobutyl ether, available from 3M. Various blends of these materials with organic solvents can be used.

The composition comprising the compounds (A), (B), optionally (C) and/or partial condensates thereof is generally applied to the substrate in amounts sufficient to produce a coating that is water and oil repellent. This coating can be extremely thin, e.g. 1 to 50 molecular layers, though in practice a useful coating may be thicker.

Suitable substrates that can be treated in a particularly effective way with the composition of this invention include substrates having a hard surface that preferably has groups capable of reacting with the compounds (A), (B), optionally (C) and/or partial condensates. Particularly preferred substrates include ceramics, glass, metal, natural and

man-made stone, thermoplastic materials (such as poly(meth)acrylate, polycarbonate, polystyrene, styrene copolymers, such as styrene acrylonitrile copolymers, polyesters, polyethylene terephthalate), paints (such as those on acrylic resins), powder coatings (such as polyurethane or hybrid powder coatings), inox, chromated steel and wood. Various articles can be effectively treated with the fluorochemical solution of the present invention to provide a water and oil repellent coating thereon. Examples include ceramic tiles, bathtubs or toilets, glass shower panels, construction glass, various parts of a vehicle (such as the mirror or windscreen), glass, and ceramic or enamel pottery materials.

Treatment of the substrates results in rendering the treated surfaces less retentive of soil and more readily cleanable due to the oil and water repellent nature of the treated surfaces. These desirable properties are maintained despite extended exposure or use and repeated cleanings because of the high degree of durability of the treated surface as can be obtained through the compositions of this invention.

To effect the treatment of a substrate, the composition as disclosed above, is applied to the substrate. The amount of compounds (A), (B), optionally (C) and/or partial condensates to be coated on the substrate will generally be that amount sufficient to produce a coating which is water and oil repellent, such a coating having at 20°C a contact angle with distilled water of at least 80°, and a contact angle with n-hexadecane of at least 40°, measured after drying and curing of the coating.

Preferably, the substrate should be clean prior to applying the compositions of the invention so as to obtain optimum characteristics, particularly durability. That is, the surface of the substrate to be coated should be substantially free of organic contamination prior to coating. Cleaning techniques depend on the type of substrate and include, for example, a solvent washing step with an organic solvent, such as acetone or ethanol.

The coating composition is typically a relatively diluted solution, containing between 0.01 and 5 percent by weight of compounds (A), (B), optionally (C) and/or partial condensates, more preferably, between 0.03 and 3 percent by weight, and most preferably, between 0.05 and 2 percent by weight.

In accordance with a preferred embodiment, compositions for application to a substrate are prepared by diluting a concentrate comprising a solution of compounds (A), (B) and optionally (C) in an organic solvent that is substantially free of water. Dilution of the concentrate may be effected by adding thereto further organic solvent. To the mixture

is also added water and optionally an acid or base catalyst to obtain the coating composition. Preferably, the concentrate from which the coating composition is prepared contains compounds (A) and (B) in their desired weight ratio to each other. In this respect, it has been found that homogeneous concentrates are preferably prepared with compounds (A) that have an alkoxy group of 2 to 4 carbon atoms as the hydrolysable groups on the silyl group. It was found that such compound more easily allow for the preparation of concentrates in which the weight ratio of compounds (B) to compounds (A) is for example between 3:1 to 12:1, preferably 6:1 to 9:1. High weight ratios may be desired in cases where a high UV stability is desired, i.e. where it is desired that the repellency properties are maintained well when the coating is exposed to UV and humidity. On the other hand, lower weight ratios, for example 1:1 to 6:1 may be desired in case transparency of the coating is critical, such as for example when coating on glass.

A wide variety of coating methods can be used to apply a composition of the present invention, such as brushing, spraying, dipping, rolling, spreading, and the like. A preferred coating method for application of the coating composition of the present invention includes spray application. An airless spray application will typically be preferred in cases where transparency of the coating is important. A substrate to be coated can typically be contacted with the treating composition at room temperature (typically, about 15°C to about 30°C). Alternatively, the mixture can be applied to substrates that are preheated at a temperature of for example between 30°C and 150°C. This is of particular interest for industrial production, where e.g. ceramic tiles can be treated immediately after the baking oven at the end of the production line. Following application, the treated substrate can be dried and cured at ambient or elevated temperature, e.g. at 40° to 300°C and for a time sufficient to dry and cure. The coating compositions of the present invention generally do not require subjecting the compositions to an elevated temperature. Thus, repellent and durable coatings in connection with this invention can be readily obtained upon coating and drying at ambient temperature. Alternatively, in addition with a thermal treatment, the coating composition may be cured by irradiation (e.g. by means of UV-irradiators, a laser, etc.) in a manner known per se, depending on the type and presence, respectively of an initiator. The process may also require a polishing step to remove excess material.

The following examples further illustrate the invention without the intention however to limit the invention thereto. All parts are by weight unless indicated otherwise.

5 1. **Synthesis of fluorinated polyether disilanes**

 A. **Fluoropolyetherdisilane FES-1:**

 FES-1 was prepared by reacting perfluoropolyetherdiester
 $\text{CH}_3\text{OC}(\text{O})\text{CF}_2\text{O}(\text{CF}_2\text{O})_{9-11}(\text{CF}_2\text{CF}_2\text{O})_{9-11}\text{CF}_2\text{C}(\text{O})\text{OCH}_3$ (with average molecular weight
10 of about 2000), commercially available from Ausimont, Italy, under the trade designation
 Fomblin™ Z-DEAL, with 3-aminopropyltrimethoxysilane, available from Aldrich Co.,
 Milwaukee, WI, as taught in US 3,810,874 (Mitsch et al.), table 1, line 6. The exothermic
 reaction proceeded readily at room temperature, simply by mixing the starting materials.
 The progress of the reaction was monitored by infrared analysis.

15

 B. **Fluoropolyetherdisilane FES-2:**

 FES-2 was prepared by reacting perfluoropolyetherdiester Fomblin™ Z-
 DEAL, with 3-aminopropyltriethoxysilane, available from Aldrich Co. Milwaukee, WI,
 essentially as taught in US 3,810,874 (Mitsch et al.), table 1, line 6. The exothermic
20 reaction proceeded readily at room temperature, simply by mixing the starting materials.
 The progress of the reaction was monitored by infrared analysis.

 C. **Preparation of FES-3 :**

 The hydrocarbon, organic starting material
25 $\text{CH}_3\text{OCOC}_2\text{H}_4\text{O}(\text{CH}_2)_6\text{OC}_2\text{H}_4\text{COOCH}_3$ was prepared by base-catalyzed Michael addition
 of 1,6-hexanediol (Aldrich, Milwaukee, WI) to two equivalents of acrylonitrile, followed
 by acid-catalyzed methanolysis. The methyl ester was directly fluorinated with F_2 to
 produce the perfluorinated derivative $\text{CF}_3\text{OCOC}_2\text{F}_4\text{O}(\text{CF}_2)_6\text{OC}_2\text{F}_4\text{COOCF}_3$. The method
 followed was essentially that found in US 5,578,278 (Fall et. al.). The crude perfluorinated
30 ester was treated with 150 mL of 14% BF_3 in methanol and agitated vigorously for 24 hrs.
 The mixture was washed with water and dried over MgSO_4 and distilled (100 - 110 °C @
 0.3 torr) to yield $\text{CH}_3\text{OCOC}_2\text{F}_4\text{O}(\text{CF}_2)_6\text{OC}_2\text{F}_4\text{COOCH}_3$.

CH₃OCOC₂F₄O(CF₂)₆OC₂F₄COOCH₃ was further reacted with two equivalents of 3-aminopropyltriethoxysilane (available from Gelest, Inc, Tulleytown, PA) in ethanol. The reaction was followed by infrared analysis, and when complete, the solvent was stripped on a rotary evaporator to yield a colorless to light tan fluid

5 (C₂H₅O)₃Si(CH₂)₃NHC(O)C₂F₄O(CF₂)₆OC₂F₄C(O)NH(CH₂)₃Si(OC₂H₅)₃ (FES-3).

D. Preparation of FES-4 :

The procedure as described for FES-3 was followed, starting with 2,2-dimethyl-1,3-propandiol and acrylonitrile to yield

10 CH₃OCOC₂H₄OCH₂C(CH₃)₂CH₂OC₂H₄COOCH₃. Upon direct fluorination, CF₃OCOC₂F₄OCF₂C(CF₃)₂CF₂OC₂F₄COOCF₃ was produced. This was reacted with 3-aminopropyltriethoxysilane to yield

(C₂H₅O)₃Si(CH₂)₃NHCOC₂F₄OCF₂C(CF₃)₂CF₂OC₂F₄CONH(CH₂)₃Si(OC₂H₅)₃ (FES-4).

15 E. Preparation of FES-5 :

Using methods similar to those described in US 5,658,962 (Moore et. al.) tetraethyleneglycol diacetate was fluorinated and methanolized to yield

CH₃OCO(CF₂OCF₂)₃COOCH₃ (b.p. 70°C/0.5 torr), plus a minor amount of CF₃OCF₂(CF₂OCF₂)₂CO₂CH₃ produced by apparent decarboxylation during fluorination.

20 The fluorinated ester was reacted with two equivalents 3-aminopropyltriethoxysilane in ethanol. The reaction was followed by infrared analysis, and when complete, the solvent was stripped on a rotary evaporator to yield a colorless to light tan fluid

(C₂H₅O)₃Si(CH₂)₃NHCO(CF₂OCF₂)₃CONH(CH₂)₃Si(OC₂H₅)₃ (FES-5).

25 F. Synthesis of FES-6 to FES-10 :

Using methods and techniques as described for the synthesis of FES-3, other perfluoropolyetherdisilanes (FES-6 to FES-10) were prepared starting from the hydrocarbon starting materials (number indicative of number average Mw), as given in table 1. The perfluorinated esters were distilled at a temperature and pressure as given in

30 table 1. Two fractions were obtained from the reaction starting from Polytetramethylene oxide 650. Accordingly, two perfluoropolyetherdisilanes FES-9 and FES-10 were

prepared from the same hydrocarbon starting material. F-NMR was used to characterize the % functionality of the perfluorinated ester.

Table 1 : synthesis of fluorochemical disilane compounds

FES	Hydrocarbon starting material	Fluorinated ester b.p°C /torr	% functionality	Fluorinated ester M _N
FES-6	Polyethyleneglycol 400 diacetate	110-35/0.05	95	856
FES-7	Polyethyleneglycol 600 diacetate	168 – 250/1.0	93	1530
FES-8	Polytetramethylene oxide 250	70-165/0.10	97	644
FES-9	Polytetramethylene oxide 650	123-165/1.0	90	950
FES-10	Polytetramethylene oxide 650	165-260/1.0	92	1470

5

2. Methods of application

Spray Application

10 The substrates were cleaned and degreased with acetone and kept at room temperature before coating. Alternatively, the substrates were preheated before coating.

(i) Spray application with air

Fluorochemical treating compositions given in the respective examples were applied onto the substrates, by spray application using a spray gun operating with air (Venturi principle).

15

(ii) Airless spray application :

The fluorochemical treating composition was supplied to the substrate, by means of a spray gun without the use of air. The composition was sprayed onto the substrates by means of a 730073 SS nozzle (available from Spraying Systems).

20

Coated samples were dried at room temperature or forced-air oven dried at a temperature between 80°C and 150°C for 30 minutes. Afterwards, excess product was polished off using a dry or wet paper wipe.

5 Dip Application

(i) *One bath dip application* : a substrate, cleaned by acetone, was dipped in a bath comprising component (B)(eg. TEOS), fluorochemical polyether disilane, acid, water and ethanol. After removal from the bath, the treated substrate was dried at room temperature for about 20 min. After drying, the excess product was removed using a dry cloth.

10

(ii) *Two bath dip application* : a substrate, cleaned by acetone, was dipped in a bath containing component (B) (eg. TEOS). The substrate was air dried at room temperature and then dipped in a second bath comprising fluorochemical polyether disilane, acid, water and ethanol. After removal from the bath, the substrate was dried at room

15 temperature for about 20 min. After drying, the excess product was removed using a dry cloth.

Flow coating

The fluorochemical treating composition was applied using a syringe or a pipette,

20 across the top of the vertical held substrate. This method is also referred to as curtain coating.

After allowing excess solution to drain away, the substrates were placed in an oven at 90°C for 15 minutes.

25 **3. Testing**

Static Contact Angles

The treated substrates were tested for their contact angles versus water and n-hexadecane using an Olympus TGHM goniometer. The values are the mean values of 4

30 measurements and are reported in degrees. The minimum measurable value for a contact angle was 20. A value <20 meant that the liquid spread on the surface.

Advancing and Receding Contact Angles

Advancing and receding contact angles were measured on nylon film, treated with the fluorochemical disilane composition at about 3% solids, by dip application (one bath). A 85 mm x 13 mm rectangular strip of nylon film was cleaned by dipping into methyl
5 alcohol and wiping with a KIMWIPE™ wiper (commercially available from Kimberly-Clark Corp., Neenah, WI), taking care not to touch the strip's surface. The strip was allowed to dry for 15 minutes. Then, using a small binder clip to hold one end of the strip, the strip was immersed in the treating solution, and the strip was then withdrawn slowly and smoothly from the solution. The coated film strip was tilted to allow any solution run-
10 off to accumulate at the corner of the strip, and a KIMWIPE™ wiper was touched to the corner to pull away the solution build-up. The coated film strip was allowed to air dry in a protected location for a minimum of 30 minutes and then was cured for 10 minutes at 121°C.

Advancing and receding contact angles were measured using a CAHN Dynamic
15 Contact Angle Analyzer, Model DCA 322 (a Wilhelmy balance apparatus equipped with a computer for control and data processing, commercially available from ATI, Madison, WI, calibrated using a 500 mg weight). An alligator clip was fastened to a piece of coated film strip about 30 mm long, and the clip and film piece were hung from the stirrup of the balance. A 30 mL glass beaker containing approximately 25 mL of water or n-hexadecane
20 was placed under the balance stirrup, and the beaker was positioned so that the coated film strip was centered over the beaker and its contents, but not touching the walls of the beaker. Using the lever on the left side of the apparatus, the platform supporting the beaker was carefully raised until the surface of water or n-hexadecane was 2-3 mm from the lower edge of the film strip. The door to the apparatus was closed, the "Configure" option
25 was chosen from the "Initialize" menu of the computer, the "Automatic" option was chosen from the "Experiment" menu, and the computer program then calculated the time for a scan. The apparatus then raised and lowered the liquid so that the scan was taken (the advancing angle was measured as the liquid moved up and over the surface, while the receding angle was determined as the liquid moved down and away from the surface of the
30 plastic film). The "Least Squares" option was selected from the "Analysis" menu, and the average receding contact angle was calculated from the scan of the film sample. Three separate films were prepared for each material to be tested as previously described. The

95% confidence interval for the average of the 3 scans was typically about 1.2°. This procedure was repeated for water and n-hexadecane.

Aging Test

5 Treated glass samples were aged in a QUV-apparatus, following the ASTM-standard G.53-84. UV fluorescent lamps of type UVB-313 were used for the light source.

The test cycle was UV-illumination without humidification for 8 hours at a temperature of about 60°C, followed by humidification without UV-illumination, for 4 hours at a temperature of about 50°C.

10

Tilt Angle

A treated substrate was placed in a Tilt Angle Instrument. 3 drops or about 100 μ liter water were placed on the surface of the treated substrate. The substrate was tilted and the angle at which the drops start rolling off the surface was reported. The values, 15 reported in degrees (°) are the mean values of 3 measurements. The maximum recordable value was 70°.

20 4. Examples

Examples 1 to 3 and Comparative Examples C-1 and C-2

In examples 1 to 3, glass was treated in a one bath dip application with a composition containing ethanol (90.0 g), FES-1 (0.1 g), 0.3 N HCL (10.0 g) and TEOS in 25 amounts given in table 2. Comparative Example C-1 was made in the same way, but without the use of TEOS. Comparative Example C-2 was made in a 2-bath dip application: glass was dipped in a bath containing 0.3% TEOS in water. The treated glass was air dried at room temperature and then dipped in a bath containing ethanol (90.0 g), FES-1 (0.1 g), and 0.3 N HCL (10.0 g). After removal from the bath, the glass samples of examples 1 to 30 and C-1 and C-2, were air dried and excess product was removed using a dry cloth. Contact angles for water and n-hexadecane and the tilt angle were measured. The results are listed in table 2.

Table 2 : Glass treated with fluorochemical disilane and TEOS

Ex No.	% TEOS	Water Contact Angle (°) Frontside/backside*	Hexadecane Contact Angle (°) Frontside/backside*	WaterTilt Angle (°)
1	0.3% TEOS	109/108	70/67	53
2	0.6% TEOS	108/115	69/68	33
3	0.9% TEOS	118/118	68/68	39
C-1	/	101/105	62/65	>70
C-2	0.3% TEOS	82/103	68/63	

Note : * To rule out any difference between the two surfaces (tin side – air side) of the glass samples, the samples were tested on both sides as indicated by frontside and backside in Table 1. In general, no major difference could be observed between the sides of the treated glass when using the compositions of the invention.

The results as given in table 2 indicate that improved water contact angles were obtained using a one-bath application compared with a two-bath application (examples versus C-2). A one-bath application comprising TEOS especially improved the dynamic water repellency (as reflected by tilt angle) of the treated samples, compared to a one-bath application without TEOS.

Examples 4 to 9

In Examples 4 to 9, glass plates were treated by spray application (with air), with compositions containing 90 g ethanol, 0.3 g or 0.6 g TEOS, 0.1 g FES-1 and 10 g acetic acid (normality as given in table 3). After drying at room temperature, the glass plates were rinsed with water. The results of contact angles are given in table 3.

Table 3 : Contact angles of glass treated with fluorochemical disilane and TEOS

Ex No	W % TEOS	HAc (N)	Contact Angle Water	Contact Angle n-Hexadecane
4	0.3	0.3	102/105	58/56
5	0.6	0.3	103/96	56/54
6	0.3	0.6	99/99	59/56
7	0.6	0.6	103/100	58/49
8	0.3	1	107/102	57/55
9	0.6	1	102/102	51/51

Note : values reported are frontside/backside

Treated glass with high oil and water repellency was obtained. The results indicated that broad experimental conditions could be used to obtain substrates with good oil and water repellency. The glass samples were not optical clear after treatment.

Example 10 and comparative example C-3

In example 10, glass plates were treated by airless spray application with a solution of 90 g ethanol, 0.1 g FES-2, 10 g of a 0.3N acetic acid solution and 0.6 g TEOS.

Comparative example C-3 was made without TEOS. After drying under airflow, the glass plates were rinsed with water. The glass plates were dried at room temperature, by airflow. The contact angles for water and n-hexadecane and the tilt angle were measured, initially and after the samples had been abraded by an Erichson cleaning machine, for 2000 cycles using the soft side of a Scotchbrite™ sponge (available from 3M) and water. The results (mean values of 6 measurements) are given in table 4.

Table 4 : contact angles of glass plates, treated with fluorochemical polyethersilane and TEOS

Ex No	Contact angle water		Contact angle n-hexadecane		Tilt angle
	Initial	Abrasion	Initial	Abrasion	Initial
10	100/94	92	50/60	50	24
C-3	75/92	75	45/50	45	51

The results indicated that glass samples with high durable oil and water repellency could be made using fluorochemical silane and TEOS mixtures. High contact angles were made, initially, but also after abrasion, indicating that highly durable coatings were made.

- 5 The samples treated with a mixture of fluorochemical silane and TEOS not only showed higher static contact angles, but especially much higher dynamic contact angles as was reflected by higher tilt angle. The glass samples, treated by airless spray were optical clear, which was an additional advantage.

10 Examples 11 to 21

- In examples 11 to 21, a mixture of 0.20 g of various fluorochemical disilanes, as indicated in table 5, 1.80 g or 0.20 g TEOS (as indicated in table 5), 1.0 g isopropanol and 10g of a stock solution containing 700 g of 95% ethanol and 35 g 2N HCl was flow coated onto glass microscope slides. The dynamic and static contact angles were measured. The results are given in tables 5 and 6 respectively.

Table 5 : Dynamic contact angles of glass plates, treated with fluorochemical disilane/TEOS

Ex No	FES	FES/TEOS	Contact Angle Water Advancing/receding	Contact Angle n-Hexadecane Advancing/receding
11	FES-3	10/90	111/92	62/50
12	FES-4	10/90	104/92	62/50
13	FES-5	10/90	102/83	58/42
14	FES-7	10/90	123/111	72/65

20

Table 6 : Static contact angles of glass plates, treated with fluorochemical disilane/TEOS

Ex No	FES	FES/TEOS	Contact Angle Water	Contact Angle n-hexadecane
15	FES-3	50/50	105	63
16	FES-4	50/50	100	57
17	FES-5	50/50	99	62
18	FES-6	50/50	116	72

19	FES-8	10/90	99	60
20	FES-9	10/90	105	63
21	FES-10	10/90	102	61

The results of both dynamic and static contact angles indicated that substrates, treated with a mixture comprising TEOS and fluorochemical disilanes, obtained by direct fluorination and having different repeating units, had good oil and water repellency.

Examples 22 to 51

Examples 22 to 51 were made to evaluate the stability of concentrated mixtures of fluorinated disilane and compound B. Therefore, mixtures were made of 4 parts FES-1 or 4 parts FES-2 with different amounts of TEOS or methyl triethoxysilane (MTEOS, available from Aldrich Co) and different water free (<100 ppm water) solvents. The composition of the mixtures is given in tables 7 (FES-1) and 8 (FES-2). All mixtures were clear after preparation. The mixtures were kept at room temperature during 3 days and were then evaluated for their stability. The results are listed in Tables 7 and 8.

15

Table 7 : Stability of concentrated mixtures of FES-1 and TEOS in solvent

Ex No	Solvent	Parts Solvent	Parts TEOS	% FC solids	Appearance
22	Ethanol	2	2	50	Clear
23	Ethanol	4	2	40	Clear
24	Ethanol	2	4	40	Clear
25	Ethanol	4	4	33	Clear
26	Ethanol	2	6	33	Clear
27	Ethanol	2	8	28.5	Clear
28	Ethanol	4	8	25	2 phases
29	Ethanol	2	10	25	2 phases
30	MIBK	2	4	40	Clear
31	MEK	2	4	40	Clear

32	Acetone	5.3	4	30	Clear
33	Acetone	2	2	50	Clear
34	Acetone	2	4	40	Clear
35	Acetone	2	10	25	Sediment
36	Acetone	1	0.3	75	Clear
37	t-butylacetate	2	4	40	Clear

The results indicated that stable high concentrated mixtures could be made from FES-1/TEOS/Solvent. These stable concentrates could be used to make the diluted application baths to treat the glass.

5

Table 8 : Stability of concentrated mixtures of FES-2 with TEOS or MTEOS in solvent

Ex No	Solvent	Parts solvent	Parts TEOS	% FC solids	Appearance mixture
<u>TEOS</u>					
38	Ethanol	2	2	50	Clear
39	Ethanol	4	2	40	Clear
40	Ethanol	2	8	28.5	Clear
41	Ethanol	2	10	25	Clear
42	Ethanol	2	14	20	Clear
43	Ethanol	2	24	13.3	Clear
44	Ethanol	2	34	10	Slightly hazy
45	Ethanol	2	74	5	2 phases
46	MEK	2	14	20	Clear
47	Acetone	2	10	25	Clear
48	Acetone	2	34	10	Slightly hazy
<u>Methyl triethoxy silane (MTEOS)</u>					
			Parts MTEOS		
49	Ethanol	2	2	50	Clear
50	Ethanol	2	10	25	Clear
51	MEK	2	10	25	Clear

The data listed in Table 8 illustrate that stable, concentrated mixtures of FES-2 and component (B) in different solvents could be made.

10

Example 52 and comparative example C-4

5 In example 52, a glass plate was treated in a one bath application with a composition containing 90 g ethanol, 0.1 g FES-1, 10 g 0.3N HCL and 0.6 g TEOS. Comparative example C-4 was treated with a similar mixture, but without TEOS added. The samples were air dried after treatment and the excess product was removed with a dry cloth. Contact angles versus water and n-hexadecane were measured initially and after the

10 samples had been aged during several aging cycles. The results are given in table 9.

Table 9 : Contact angles of glass treated with fluorochemical disilane/TEOS – aging

Aging (hours)	Ex 52	C-4	Ex 52	C-4
	Contact angle water	Contact angle water	Contact angle n-hexadecane	Contact angle n-hexadecane
/	112	103	68	64
24	105	107	58	60
48	91	90	52	58
72	92	90	60	50
96	92	82	58	57
168	92	67	59	48
216	91	77	55	56
264	93	70	46	48
360	93	70	50	37
576	90	72	44	33
744	75	48	47	26
912	90	58	48	13

15 The results indicated that samples treated with fluorochemical disilane and TEOS exhibit high UV and humidity stability as was reflected by the contact angles, measured after severe UV/humidity aging.

Claims:

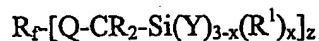
1. A composition comprising:

A. at least one fluorochemical polyether silane compound having a polyfluoropolyether segment and at least two silane groups $-\text{Si}(\text{Y})_{3-x}(\text{R}^1)_x$ per molecule,

wherein R^1 represents an alkyl group, Y represents a hydrolysable group and x is 0 or 1; and

B. a substantial amount of one or more non-fluorinated compounds of an element M selected from the group consisting of Si, Ti, Zr, B, Al, Ge, V, Pb, Sn and Zn and having at least two hydrolysable groups per molecule.

2. A composition according to claim 1 wherein said fluorochemical polyether silane compound (A) corresponds to the formula:



wherein R_f represents a multivalent polyfluoropolyether segment, Q represents an organic divalent linking group, R^1 represents a C_1 - C_8 alkyl group, Y represents a hydrolysable group, R represents hydrogen or an alkyl group of 1 to 4 carbon atoms whereby the R groups may be the same or different, z is 2, 3 or 4 and x is 0 or 1.

3. A composition according to claim 1 wherein said component (B) is a compound according to the formula:



wherein R^2 represents a non-hydrolysable group, M represents an element selected from the group consisting of Si, Ti, Zr, B, Al, Ge, V, Pb, Sn and Zn, p is 3 or 4 depending on the valence of M, q is 0, 1 or 2, and Y^1 represents a hydrolysable group.

4. A composition according to claim 1 further comprising a crosslinking agent (C).

5. A composition according to claim 4 wherein the crosslinking agent (C) is a compound of an element M^1 that is selected from the group consisting of Si, Ti, Zr, B, Al, Ge, V, Pb, Sn and Zn, said crosslinking agent (C) further having at least one hydrolysable

group and at least one reactive functional group per molecule that is capable of engaging in a crosslinking reaction.

6. The composition according to claim 1, wherein the hydrolysable groups in
5 components (A) and (B) may be the same or different and are independently selected from a halide group, an alkoxy group, an acyloxy group, an aryloxy group or a polyoxyalkylene group.
7. The composition according to claim 1, wherein the polyfluoropolyether segment
10 includes perfluorinated repeating units selected from the group consisting of $-(C_nF_{2n}O)-$, $-(CF(Z)O)-$, $-(CF(Z)C_nF_{2n}O)-$, $-(C_nF_{2n}CF(Z)O)-$, $-(CF_2CF(Z)O)-$, and combinations thereof, wherein Z is a perfluoroalkyl group, an oxygen-substituted perfluoroalkyl group, a perfluoroalkoxy group, or an oxygen-substituted perfluoroalkoxy group, all of which can be linear, branched, or cyclic, and have 1 to 9 carbon atoms and 0 to 4 oxygen atoms and
15 wherein n is a number from 1 to 12 inclusive.
8. The composition according to claim 1, wherein the weight ratio of component (A) to component (B) is 1:1 to 1:20.
- 20 9. The composition according to claim 1 further comprising water and an acid or base catalyst.
10. The composition according to claim 1 wherein said composition further comprises organic solvent and component (A) is present in an amount between 0.01% by weight and
25 5% by weight based on the total weight of the composition and component (B) is present in an amount of 0.01% by weight and 5% by weight based on the total weight of the composition.
11. The composition according to claim 1 further comprising an organic solvent and
30 being substantially free of water

12. The composition of claim 11 comprising organic solvent in an amount of not more than 50% by weight based on the total weight of the composition.
13. The composition of claim 11 wherein the weight ratio of component (A) to component (B) is between 1:1 and 1:9.
14. A composition derivable from a partial condensation reaction of a composition as defined in claim 1.
15. Method of treating a substrate comprising applying on at least part of a surface of said substrate a composition as defined in claim 1.
16. Method of making a composition according to claim 14 comprising the steps of:
- (a) providing a mixture of components (A), (B) and optionally (C);
 - (b) allowing components (A), (B) and (C) to react to form a partial condensate.
17. Method according to claim 16 wherein said mixture (a) is provided by diluting a composition as defined by any of claims 11 to 13 such that the amount of components (A) and (B) is in the range of 0.01 to 5% by weight based on the total weight of the diluted composition and further adding thereto water and optionally a base or acid catalyst.
18. Method according to claim 16 further including the step of allowing said substrate to dry at a temperature between 15 and 30°C.
19. Coated substrate obtainable by the method of claim 15.
20. A composition comprising a fluorinated compound of the formula:
- $$X(CF_2)_n-O-C_{n'}F_{2n'}-O-(CF_2)_n X$$
- where n is 1 to 6 inclusive,; n' is 5 to 12 inclusive, X is selected from the group consisting of -COOH, -COOM_{1/2}, -COONH₄, -COOR, -CH₂OH, -COF, -COCl, -COR', CONR'R',

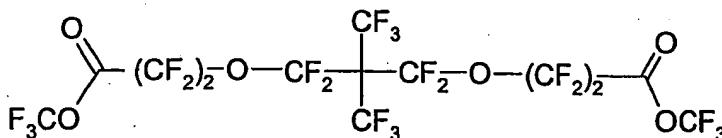
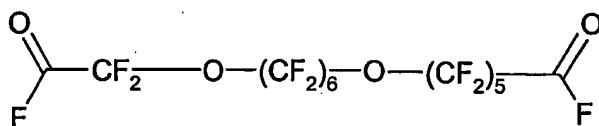
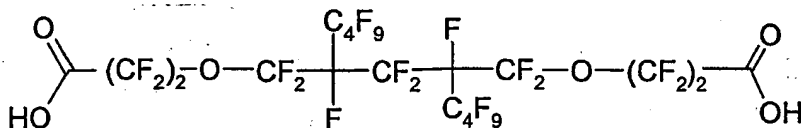
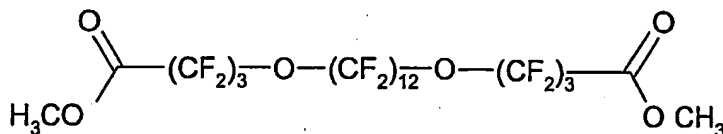
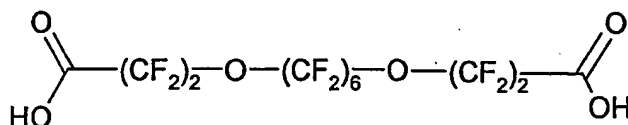
-CH₂NH₂, -CH₂NCO, -CN, -CH₂OSO₂R, -CH₂OCOR, -OC(O)CH₃, -CH₂OCOCR'=CH₂,
-CONH(CH₂)_mSi(OR)₃, -CH₂O(CH₂)_mSi(OR)₃; where

M is an ammonium radical or a metal atom having a valence "v" of 1 to 4,

each R is independently selected from the group consisting of alkyl groups having from 1
5 to 14 carbon atoms, fluoroalkyl groups having from 1 to 14 carbon atoms, aryl groups
having from 6 to 10 ring-carbon atoms, and heteroatom-containing groups having from 1
to 14 carbon atoms, and m is an integer from 1 to 11;

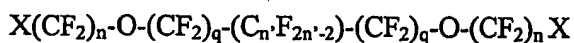
R' is independently H or R, with the proviso R' is not a fluoroalkyl group.

10 21. The composition according to claim 20, wherein the fluorinated compound is:



20

22. A composition comprising a fluorinated compound of the formula:



where

n is 1 to 6 inclusive;

C_nF_{2n-2} represents a cycloalkylene moiety where n' is 5 to 7 inclusive,

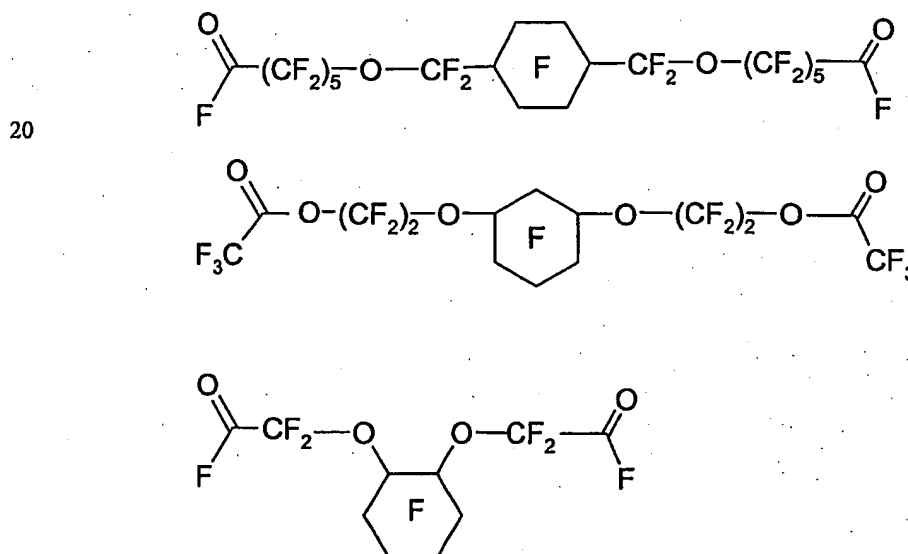
- 5 X is selected from the group consisting of -COOH, -COOM_{1/v}, -COONH₄, -COOR, -CH₂OH, -COF, -COCl, -COR', CONR'R', -CH₂NH₂, -CH₂NCO, -CN, -CH₂OSO₂R, -CH₂OCOR, -OC(O)CH₃, -CH₂OCOCR'=CH₂, -CONH(CH₂)_mSi(OR)₃, -CH₂O(CH₂)_mSi(OR)₃; where M is an ammonium radical or a metal atom having a valence "v" of 1 to 4,

- 10 each R is independently selected from the group consisting of alkyl groups having from 1 to 14 carbon atoms, fluoroalkyl groups having from 1 to 14 carbon atoms, aryl groups having from 6 to 10 ring-carbon atoms, and heteroatom-containing groups having from 1 to 14 carbon atoms,

q is 0 or 1, and m is an integer in the range from 1 to 11;

- 15 R' is independently H or R with the proviso R' is not a fluoroalkyl group.

23. The composition according to claim 22, wherein the fluorinated compound is:



INTERNATIONAL SEARCH REPORT

In ☐ International Application No
PCT/US 02/28312

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C09D183/00 C09D183/04 C09K3/00 C08J5/00 C08G77/00
C08G65/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09D C09K C08J C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, PAJ, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 306 758 A (PELLERITE MARK J) 26 April 1994 (1994-04-26) cited in the application column 3, line 19 - column 4, line 65 column 9, line 3 - line 23; claims 1,4,5,9,10,13; examples 1-14 ---	1-3,6-8, 10-15, 19-21
X	US 3 810 874 A (MITSCH RONALD ALLEN ET AL) 14 May 1974 (1974-05-14) column 1, line 49 - column 2, line 72 column 7, line 41 - line 63; example 28; table 1 --- -/-	1-3,6-8, 10-15, 19-21

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

A document defining the general state of the art which is not considered to be of particular relevance

E earlier document but published on or after the international filing date

L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

O document referring to an oral disclosure, use, exhibition or other means

P document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

G document member of the same patent family

Date of the actual completion of the international search

20 November 2002

Date of mailing of the international search report

27/11/2002

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Kiebooms, R

INTERNATIONAL SEARCH REPORT

In Application No

PCT/US 02/28312

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 6 273 348 B1 (KAWASHIMA KENICHI ET AL) 14 August 2001 (2001-08-14) column 3, line 21 -column 4, line 5 column 5, line 21 -column 8, line 17 column 15, line 16 - line 67; claims 8,10-12 ---	1-23
Y	EP 0 797 111 A (SONY CORP) 24 September 1997 (1997-09-24) page 2, line 3 - line 20 page 4, line 22 -page 5, line 35; claim 1 ---	1-23
Y	US 4 024 306 A (TAKAMIZAWA MINORU ET AL) 17 May 1977 (1977-05-17) column 1, line 45 -column 4, line 16; claims 1-17; examples 1-5 -----	1-23

INTERNATIONAL SEARCH REPORT

Information on patent family members

In: International Application No

PCT/US 02/28312

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5306758	A	26-04-1994	AU 632869 B2	14-01-1993
			AU 6669890 A	20-06-1991
			BR 9006319 A	24-09-1991
			CA 2030221 A1	15-06-1991
			DE 69025151 D1	14-03-1996
			DE 69025151 T2	19-09-1996
			EP 0433070 A2	19-06-1991
			ES 2081949 T3	16-03-1996
			JP 3009744 B2	14-02-2000
			JP 3258863 A	19-11-1991
			KR 178513 B1	01-04-1999
US 3810874	A	14-05-1974	CA 960222 A2	31-12-1974
			CA 960221 A1	31-12-1974
			CA 960400 A1	31-12-1974
			GB 1309401 A	14-03-1973
			US 3845051 A	29-10-1974
			AU 462798 B	10-07-1975
			AU 3317471 A	15-03-1973
			AU 469118 B	05-02-1976
			AU 3317671 A	15-03-1973
			BE 772308 A1	07-03-1972
			BE 772309 A1	07-03-1972
			DE 2145174 A1	23-03-1972
			DE 2145176 A1	16-03-1972
			FR 2106375 A5	05-05-1972
			FR 2116364 A5	13-07-1972
			GB 1373931 A	13-11-1974
			GB 1373932 A	13-11-1974
			IT 939387 B	10-02-1973
			IT 939388 B	10-02-1973
			JP 1408932 C	24-11-1987
			JP 59191721 A	30-10-1984
			JP 62014169 B	01-04-1987
			JP 1408933 C	24-11-1987
			JP 59191722 A	30-10-1984
			JP 62014170 B	01-04-1987
			JP 60034924 A	22-02-1985
			JP 59191723 A	30-10-1984
			JP 1408934 C	24-11-1987
			JP 59191724 A	30-10-1984
			JP 62014171 B	01-04-1987
			JP 1322347 C	11-06-1986
			JP 59191725 A	30-10-1984
			JP 60050823 B	11-11-1985
			JP 59030724 B	28-07-1984
			JP 51002083 B	23-01-1976
			JP 1509565 C	26-07-1989
			JP 62048724 A	03-03-1987
			JP 63061336 B	29-11-1988
			NL 7111865 A	10-03-1972
			NL 7112315 A ,B	10-03-1972
			US 4094911 A	13-06-1978
			US 3972856 A	03-08-1976
			US 4085137 A	18-04-1978
			BE 747087 A1	09-09-1970
			CA 960397 A1	31-12-1974
			DE 2011774 A1	17-09-1970

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 02/28312

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 3810874	A		DE 2066042 B1	22-11-1979
			FR 2037807 A5	31-12-1970
			GB 1309402 A	14-03-1973
			NL 7002813 A ,B,	14-09-1970
US 6273348	B1	14-08-2001	JP 11311168 A	09-11-1999
			DE 19919413 A1	04-11-1999
			US 2001042801 A1	22-11-2001
			US 2001032896 A1	25-10-2001
EP 0797111	A	24-09-1997	JP 9255919 A	30-09-1997
			EP 0797111 A2	24-09-1997
			US 5922787 A	13-07-1999
US 4024306	A	17-05-1977	JP 873672 C	29-07-1977
			JP 50126033 A	03-10-1975
			JP 52001926 B	19-01-1977